

Zeeman splitting of shallow donors in GaN

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The Zeeman splitting of the donor spectra in cubic- and hexagonal-GaN are studied using an effective mass theory approach. Soft-core pseudopotentials were used to describe the chemical shift of the different substitutional dopants. The donor ground states calculated range from 29.5 to 33.7 meV, with typically 1 meV higher binding in the hexagonal phase. Carbon is found to produce the largest donor binding energy. The ionization levels and excited states are in excellent agreement with Hall and optical measurements, and suggest the presence of residual C in recent experiments.

Shallow donors in III-N semiconductors are one of the key fundamental elements in the fabrication of short-wave length optical and high-frequency electronic devices.¹ Despite the great activity and considerable progress on the growth quality and characterization of these materials, the origin of the n-type conductivity in nominally undoped GaN is still not well established. Native defects, such as N vacancies, and residual impurities like O and Si have been invoked as the prime sources of the high electron concentrations ($\sim 10^{17} \text{ cm}^{-3}$) seen in experiments.^{2,3} However, the donor ionization levels introduced are not fully known. Temperature dependent transport experiments have indicated binding energies of about 36 meV for residual donors and 26 meV for Si.⁴ Recent Hall effect measurements for high-energy electron-irradiated GaN/sapphire samples suggest the appearance of a donor state from the N vacancy with a donor energy of about 64 meV, much larger than the value expected for residual donors.⁵ Study of electronic excitations by Raman scattering of unintentional donors gives energies ranging from 18.5 to 30 meV for cubic and hexagonal GaN.⁶ Although O is known to display a shallow level state, it behaves as a deep donor under high hydrostatic pressure ($> 20 \text{ GPa}$). However, this is not the case for Si.⁷

Arrhenius plot analyses of the electron concentration of O- and Si- implanted in GaN yields activation energies of about 29 meV for both dopants.³ On the other hand, magneto-transmission measurements of Zeeman splitting of the donor spectra in Si-doped GaN films are a bit higher, and consistent with other reports.⁸ However, more recent infrared spectroscopy studies of the Zeeman splitting of donors in undoped GaN grown by hydride vapor phase epitaxy (HVPE) show $1s - 2p_{\pm}$ transitions at 23.3 and 25.95 meV (in the limit of zero magnetic field),

apparently due to two different donor species.⁹ Ground states at 31.1 and 33.8 meV, respectively, were inferred from these transitions. While the lower transition was believed to come from Si, the origin of the larger one was unclear.

Carbon is known to be an amphoteric impurity in GaN, but it is widely believed to predominantly introduce acceptor levels. Recent quantum molecular dynamics calculations by Boguslawski *et al.*¹⁰ showed that C substituting in the Ga site gives rise to shallow donor states. Although the formation energy estimates indicated that C atoms do prefer to occupy the N site, there is still the possibility that some C atoms will be incorporated into the Ga vacancies. In these calculations, C was found to have also an excellent solubility, and an efficient self-compensation of acceptors by carbon donors.¹⁰ Moreover, Zhang *et al.*¹¹ have recently reported photoluminescence experiments of C-doped GaN which clearly demonstrate that the incorporation of carbon can produce a significant yellow luminescence, and that there is a continued C-compensation by the generation of additional shallow donors.

In this work we calculate binding energies for substitutional donor impurities for different species. Our results indicate that residual carbon in GaN films could indeed give rise to additional shallow donors with binding energy close to those previously assigned to Si and O. To our knowledge, the essential effect of central cell corrections for the different impurities on the donor ionization levels in GaN has not been discussed before. We also introduce here the effective mass anisotropy in wurtzite GaN, which is shown to be important in the calculation of impurity states.

The purpose of this letter is then twofold. First, we report effective mass theory (EMT) calculations of the binding energy of Si, O and C shallow donors in GaN for both crystal phases, cubic (zincblende) and hexagonal (wurtzite). In this EMT calculations, the anisotropy of the conduction band and the dielectric constant for h-GaN are explicitly included. Furthermore, the central cell corrections introduced by the different impurities are taken into account via soft-core atomic pseudopotentials. The second purpose is to examine the Zeeman splitting of the excited states of substitutional impurities under the presence of an external magnetic field, and to compare our estimates with the available experimental results.

Near the Γ point ($k = 0$), the lower conduction band¹² in hexagonal GaN is ellipsoidal, with different longitudinal and transverse (with the c-axis) effective masses

(which are clearly equal in the cubic phase). Within effective mass theory, and neglecting spin splitting,¹³ the Hamiltonian for the envelope wave function under an external magnetic field along the \hat{z} -axis (parallel to the crystal c-axis), is given by

$$H = -\frac{\hbar^2}{2m_{\perp}^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{\hbar^2}{2m_{\parallel}^*} \frac{\partial^2}{\partial z^2} + \mu_{\perp}^* L_z B_z + \frac{\pi \mu_{\perp}^* B_z^2}{2\Phi_o} (x^2 + y^2) + U(r), \quad (1)$$

where we have used a symmetric gauge, μ_{\perp}^* is the effective Bohr magneton, $\mu_{\perp}^* = e\hbar/2m_{\perp}^*c$, and L_z is the orbital momentum operator along the principal axis (in units of \hbar). Here, $\Phi_o = hc/e$ denotes the magnetic flux quantum, and $U(r)$ is the impurity-donor potential defined as the difference between the bare pseudopotential of the impurity and that of the host atom.¹⁴ The pseudopotentials we use here are those of Jansen and Sankey,¹⁵ who fitted to the functional form of Bachelet-Hamann-Schlüter fame.¹⁶ These pseudopotentials consist essentially of two parts. A local short-range angular-momentum-dependent potential $V_l(r)$, and a long-range core potential $V_{core}(r)$, where

$$V_l(r) = \sum_{i=1}^3 [A_i(l) + r^2 A_{i+3}(l)] e^{-\alpha_i(l) r^2}, \quad (2)$$

and

$$V_{core}(r) = -\frac{Z_v}{r} \sum_{i=1}^2 C_i \text{erf}[(\alpha_i^{core})^{1/2} r]. \quad (3)$$

Here, $A_i(l)$, $\alpha_i(l)$, C_i and α_i^{core} are the fitting parameters to *ab initio* pseudopotentials, with Z_v denoting the valence charge. This type of pseudopotential has been used widely and with great success in calculations of the electronic and structural properties of semiconductors.¹⁵ The extremely good transferability of these pseudopotentials in the description of atoms in different chemical environments has been discussed before by Goedecker *et al.*,¹⁷ and is related to the existence of an inert region around the nucleus, essentially independent of the chemical environment.

The envelope eigenfunctions $F(r)$ of the Hamiltonian in Eq. (1) are obtained in a variational approach, and chosen here to be an expansion of spherical harmonics and a linear combination of hydrogenic radial functions such that $F(r) = \sum B_j r^l e^{-\beta_j r} Y_{lm}(\theta, \phi)$. The donor energy levels are then obtained using the sets $\{B_j\}$ and $\{\beta_j\}$ of variational parameters.

For c-GaN (zincblende), we have used a reliable theoretical value of the isotropic effective mass for the conduction band ($m_c^* = 0.19 m_o$),¹⁸ while for the dielectric constant we have used the experimental (and isotropic) value of $\epsilon_o = 9.5$.¹ [Notice that m_c^* is not known experimentally.] On the other hand, for the hexagonal

(wurtzite) phase of GaN we have used the experimental (and theoretical¹⁸) value of $m_{\perp}^* = 0.22 m_o$,^{9,19} and the theoretical value $m_{\parallel}^* = 0.19 m_o$,¹⁸ for the parallel mass. In this case the dielectric constant is obtained from the combination $\epsilon_o^* = (2\epsilon_{\perp}^{-1}/3 + \epsilon_{\parallel}^{-1}/3)^{-1} = 9.8$, where ϵ_{\perp} and ϵ_{\parallel} are set to the experimental values of 9.5 and 10.4, respectively.²⁰ Due to the moderately polar behavior of these materials, the effect of the electron-phonon interaction on the shift of the energy levels is considered through a polaron correction. A Fröhlich coupling constant of $\alpha_F = 0.49$ has been fixed for both crystal phases. This value gives rise to an 8% enhancement of the donor states.²¹

Figure 1 shows a plot of the position of the electronic transitions $1s - 2p_o$ and $1s - 2p_{\pm}$ as a function of magnetic field B for O and C donors in h-GaN. The field is parallel to the c-axis direction. The ground state and transitions to the first excited states at zero field are shown in Table I. For O we find a ground state energy of 31.4 meV, and 33.7 for C, with internal transition energies $1s - 2p_{\pm}$ at 23.3 meV and 25.1 meV respectively. These values are in excellent agreement to those found by Moore *et al.*⁹ at 23.3 and 25.9 meV. Notice we have used the same effective mass ($m_{\perp}^* = 0.22 m_o$) and dielectric constant ($\epsilon_o^* = 9.8$) as those authors. However, they assumed that the lower transition arises from Si donors while the higher one was associated with a second donor of unknown origin, presumably O. As we show in Table I, Si has an EMT ionization energy of 30.4 meV with a $1s - 2p_o$ transition (which does not shift appreciably with field) at 22.8 meV. These results would indicate that the binding energy attributed in Ref. [9] to Si is probably due to O, and that the second donor may be indeed due to residual C-impurities. Since residual C was not detected, and the samples were growth by HPVE with no carbon sources, it would seem unlikely that carbon donors would be present. However, as we mentioned in the introduction, small C concentrations of $\leq 2 \times 10^{16} \text{ cm}^{-3}$ have been found in unintentionally doped samples grown by HPVE.¹¹ Those concentrations were below the detection limit of the secondary ion-mass spectroscopy (SIMS), but well within the photoluminescence limits.¹¹ This would indicate that similar SIMS non-detection of C impurities in samples obtained by other growth techniques does not unequivocally prove the absence of small quantities of this donor species, allowing our identification to be correct. Carefully monitored C doping together with infrared absorption measurements would be needed to clarify this point.

We would like to point out that the transition $1s - 2p_{\pm}$ we find in Si at 22.3 meV, is in good agreement with the transition at 21.7 meV observed by Wang *et al.*⁸ by infrared absorption spectroscopy of purposely Si-doped GaN grown by HVPE. Since the linewidths observed were rather large (~ 5 meV) compared with widths reported for nominally undoped samples,²² it is likely that the small difference of 0.6 meV here is within the uncertainty

of the peak position measured.

Notice also that due to the anisotropy of the effective mass and dielectric constant in the wurtzite phase of GaN, the $2p_o$ and $2p_{\pm}$ states are non-degenerate even at zero field. This effect is exhibited in Figure 1 as a shift on the transition energy of about 0.5 meV for both impurities. Notice that in Ref. [9] a transition at about 17 meV has also been observed, which remained unaffected as the magnetic field was turned on. That feature was assigned to the $1s - 2p_o$ transition of the donor with 31.1 meV binding energy, arguing that its origin was related to the non-isotropic conduction band of GaN. As we can observe in Table I and Figure 1, our EMT calculations indicate that such kind of transition does not exist in either donor considered here. Since the associated binding energy of such state would be much smaller, the identity of that species is not any of the obviously present, and it remains a puzzle.

In Figure 2 we show the transition energy for O and C donors as a function of the magnetic field for c-GaN. As seen there and in Table I, the ionization levels for this phase are close to those of the hexagonal-GaN. We find that the difference between the two phases is typically 1 meV for each donor, being larger in the hexagonal-GaN host, partly due the larger effective mass. Notice also that the $1s - 2p_o$ and $1s - 2p_{\pm}$ transitions are all degenerate at zero magnetic field, as one expects in this isotropic-band system. Unfortunately, no definitive experimental results exist yet for the shallow donor levels in c-GaN with which to compare our results.²³

Finally, we should mention that in all our EMT calculations we have employed (were available) the experimental values of the effective mass and dielectric constant for GaN. We find that donor levels are somewhat sensitive to the variation of these parameters. For example, an uncertainty of $\pm 0.01m_o$ ¹⁹ in the conduction effective mass would yield a change of less than ± 1.5 meV on the energy levels. Notice, however, that all energy levels and transitions shown in Table I would shift correspondingly, maintaining the relative position for the different impurities, which helps in the determination of their identity (e.g., largest binding energy for C).

To conclude, let us also mention that we find that Ge donors show a spectrum very similar to that found in Si.

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c-GaN			h-GaN			
Si	O	C	Si	O	C	
1s	29.5	30.4	32.5	30.4	31.4	33.7
1s - 2p _±	21.8	22.7	24.4	22.3	23.3	25.1
1s - 2p _o	21.8	22.7	24.4	22.8	23.7	25.6
1s - 3p _o	26.1	26.9	29.0	27.0	28.0	30.1

TABLE I. Ground state 1s and lower few internal transitions for different impurities in GaN for both crystalline phases, zincblende (cubic), and wurtzite (hexagonal). Magnetic field is zero here. All energies are in meV.

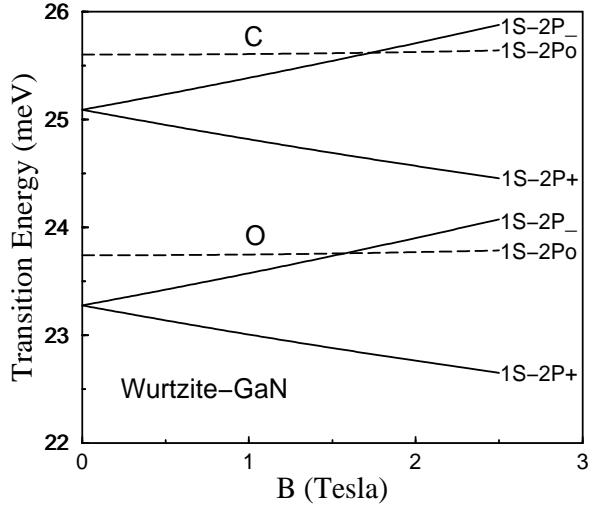


FIG. 1. Zeeman splitting for O and C shallow donors in hexagonal GaN. Magnetic field is applied parallel to the c-axis. Anisotropy in the effective mass leads to a shift of the $1s - 2p_o$ transition line at $B = 0$, while transitions $1s - 2p_{\pm}$ are degenerate.

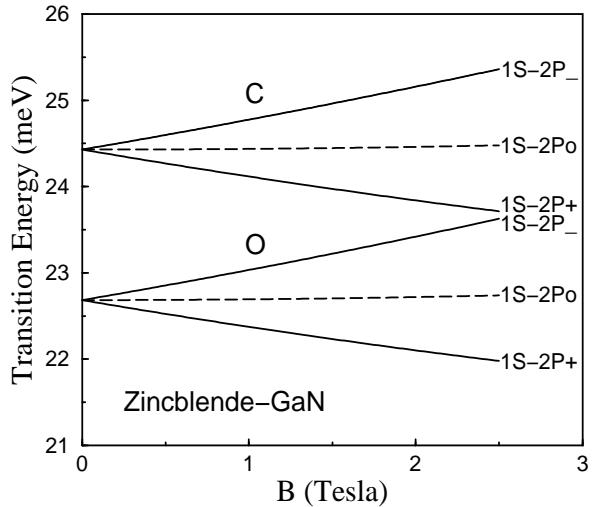


FIG. 2. Zeeman splitting for O and C shallow donors in cubic GaN. Magnetic field is applied parallel to a symmetry axis. Isotropy of the effective mass in this case yields the same value for the $1s - 2p_o$ and $1s - 2p_{\pm}$ transitions at $B = 0$. At $B \neq 0$ the transitions $1s - 2p_{\pm}$ split accordingly.